Titaniferous–Ferruginous Laterite of Meyer Lake, Molokai, Hawaii[1]

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THE SOILS belonging to the ferruginous humic latosol group in the Hawaiian Islands have accumulated titanium oxide in or near the surface horizon of the soil profile. Cline *et al.* (in press) have separated this group of soils on this basis in their classification of Hawaiian soils. Sherman (1949, 1952) has shown that these soils have progressively accumulated iron and titanium oxide with soil weathering age. A highly weathered soil, rich in titanium oxide, would represent the anatase-leucoxene stage of the weathering sequences described by Jackson *et al.* (1948). This weathering stage would include anatase and leucoxene, which are hydrated amorphous titanium oxides according to Carroll and Woof (1951), both products of the weathering synthesis mechanism and ilmenite, brookite, and rutile of the weathering residue mechanism, Jackson and Sherman (1953).

During 1952 and 1953 the guava and other shrubs were cleared from a large area of land around Meyer Lake on the island of Molokai for the purpose of pasture improvement. The entire area was plowed, exposing areas of soils of extremely high titanium content. Many of these titanium-rich areas occurred as indurate dehydrated areas which are easily detected by their grayish purple color as compared to the reddish brown color of the surrounding area. A closer examination of these indurate areas revealed that they contained numerous, magnetic ferruginous concretions. The development of these concretions indicated a movement of iron in solution from the surrounding area and its redeposition from either near-surface percolating water or ascending water from the subsoil. The occurrence of the indurate areas cannot be attributed entirely to a difference in degree of slope, but rather to areas where exposure of sufficient magnitude has occurred to cause the dehydration of the hydrated oxides. The concretionary indurate soil horizons usually occurred on a gentle slope with a majority of them occurring near the foot of the slope. The accumulation of concretions appeared to be the result of micro relief in the slope or retardation of percolating waters due to reduced porosity of the soil.

It was also observed that some movement of soil aggregates and concretions did occur as the result of erosion. These could be found at the foot of the steep slope directly west of Meyer Lake. The deposits of these materials were quite distinct from the concretionary indurate layers. The latter is due to synthesis mechanism, whereas the deposits near Meyer Lake are mechanically sorted materials having different physical characteristics. They are recent deposition resulting from the removal of cover and subsequent rains.

The exposure of the area around Meyer Lake has given an excellent opportunity to

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study the condition which led to the accumulation of iron and titanium oxides in these dehydrated areas. It also offers an excellent site for the study of the movements of these oxides, and the nature of the minerals in which the oxides become stable constituents of the concretions and surface soil.

EXPERIMENTAL PROCEDURES

The soil samples were selected to give the following information: (a) The chemical composition of a typical titaniferous-ferruginous laterite profile which occurs in the indurate areas near Meyer Lake; (b) The extent of the movement of iron and titanium in solution and the nature of their deposition products by collecting samples; (c) The chemical composition of ferruginous aggregates and concretions deposited along the shore of Meyer Lake by erosion.

The representative profile was selected in a road cut on the slope above Meyer Lake. The soil belongs to the Naiwa family of the ferruginous humic latosol group. The description of this profile is as follows:

A Horizon—0 to 12 inches. Grayish purple, concretionary, slaglike, massive, indurate layer having a high bulk density. The concretions vary in size from that of a common pinhead to half an inch in diameter. Both soil and concretions are strongly magnetic. It is obvious that this horizon has accumulated iron and titanium oxides of high specific gravity.

B Horizon—12 to 20 inches. A reddish brown, friable, non-plastic silty clay loam.

C Horizon—20 to 34 inches. Rotten, fine grain, grayish lava rocks mixed with reddish brown silty clay soil. The rock was in various stages of weathering and would crumble easily by pressing in one's hand.

D Horizon—below 34 inches. Bluish gray clay which had a greasy consistency when wet.

Samples from this profile were analyzed by procedures described by Piper (1944).

A series of samples was collected in a line across an indurate area as shown in Figure 1. The indurate layer is identified readily by the grayish purple color and the hydrated soil by its reddish brown color. Two of the soil sampling sites, A and B, at the top of the slope, and one site, H, were from hydrated soil and five sampling sites were from the dehydrated indurate area. The five samples from the dehydrated area were separated into concretions and soil by screening. The analysis for oxides, as described by Piper (1944), was used to determine the chemical composition of these soils. The analysis for ilmenite, iron titanate, was made by an adaptation of a procedure described by Thompson (1952). The ferrous iron was determined volumetrically by titration with a standard potassium dichromate solution using barium diphenylamine sulphonate as an indicator after digestion of sample in $HF–H_2SO_4$ and dilution with a mixture of boric, phosphoric, and sulfuric acids. Ferric iron was determined by dissolving the $KHSO_4$ fusion cake with a 10 per cent H_2SO_4 solution, treatment with $SnCl_2$ and an excess $HgCl_2$, and titrated with standard potassium dichromate.

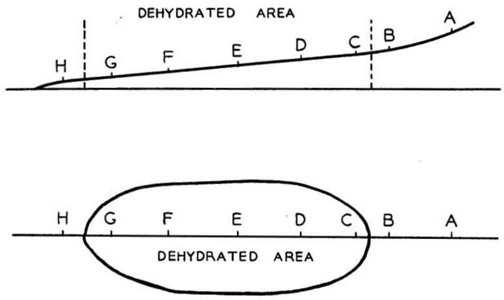

Fig. 1. Vertical and horizontal sketches of sampling sites on line across a dehydrated area near Meyer Lake.

Samples collected from the erosional deposits along the shore of Meyer Lake were analyzed in the same manner.

EXPERIMENTAL RESULTS

The chemical composition of the typical soil profile of the Naiwa family of the ferruginous humic latosol is given in Table 1.

TABLE 1
THE CHEMICAL COMPOSITION OF A TITANIFEROUS-FERRUGINOUS LATERITE LOCATED ON SLOPE TO MEYER LAKE, MOLOKAI

DESCRIPTION	DEPTH INCHES	SiO_2 PER CENT	Al_2O_3 PER CENT	Fe_2O_3 PER CENT	TiO_2 PER CENT	MnO PER CENT
Surface—grayish purple indurate layer rich in ferruginous concretions	0–12	8.78	12.16	45.98	19.22	0.19
Friable reddish brown silty clay	12–20	12.03	16.70	41.64	19.56	0.17
Rotten gray lava rock—weathered	20–34	24.80	47.10	6.60	9.20	0.22
Bluish gray silty clay	34+	17.69	46.16	12.84	2.03	0.07

The analysis of this profile shows that the chemical composition is similar to that of the soils of other profiles of the Naiwa family as reported by Sherman *et al.* (1949) and Sherman (1949, 1952). The iron oxide and titanium oxide contents were found to be high in the soil solum, being 46 and 42 per cent for iron oxide and 19 and 20 per cent for titanium oxide. The low silica content and the absence of alumino-silicate minerals, montmorin and kaolin, indicate the degree of the intensity of chemical weathering. Desilication has progressed to the point where these minerals have decomposed. The chemical composition of the rotten lava is similar to that found in other locations. Differential thermal analysis identified kaolin as the dominant mineral in the weathered material adjacent to the rotten rock.

The data presented in Table 2 show the chemical composition of the samples taken across the indurate area, Figure 1. The titanium oxide content of the samples ranged from 10.2 to 20.6 per cent with the highest levels occurring within the dehydrated indurate area. The titanium oxide content of the concretions was approximately one-half of that found in the soil of the same sampling site. The concretions retained on a 40-mesh screen amounted to 30 to 43 per cent of the weight of the soil. The iron oxide content of the soil ranged from 33.1 to 57.4 per cent in the indurate area as compared to 21.4 to 37.6 per cent in the hydrated reddish brown soils. The iron oxide content of the concretions was very high, ranging from 65.7 to 74.6 per cent. Aluminum oxide content of the soil and the concretions from the indurate area was very low. The silica content of the concretions was extremely low with 4.1 per cent being the greatest percentage found.

The ferrous and ferric iron contents of the soil were determined in order to estimate the percentage of ilmenite present in the soil. The iron occurring in ilmenite ($FeO \cdot TiO_2$) is in the ferrous form. One can assume that the ferrous iron in the soil may exist in the mineral ilmenite provided weathering has progressed under conditions of excellent oxidation and drainage. However, it is known that ferrous iron can exist in other minerals common to advanced stages of weathering such as magnetite ($2\ FeO \cdot Fe_2O_3$). The results of the ferrous and ferric iron determination are given in Table 3.

The data in Table 3 show that the ferrous iron content of the concretions is much lower than that found in the soil. The ferrous iron content of the concretions was 3.3 and 4.1 per cent; in the soil it ranged from 12.0 to 14.8 per cent. When the ilmenite content is calculated from the ferrous iron content, there is an excess of free titanium oxide in the concretion. Some free titanium oxide does

TABLE 2
THE CHEMICAL COMPOSITION OF SERIES OF SAMPLES TAKEN AT INTERVALS ALONG A LINE CROSSING A DEHYDRATED TITANIFEROUS–FERRUGINOUS LATERITE AREA ON A SLOPE OF A HILL NEAR MEYER LAKE, MOLOKAI

PROFILE SITE ON SLOPE	DESCRIPTION	DEPTH INCHES	SiO_2 PER CENT	Al_2O_3 PER CENT	Fe_2O_3 PER CENT	TiO_2 PER CENT	MnO PER CENT
A.......	Reddish brown granular material having a high bulk density...........	0–9	20.72	13.00	21.40	14.80	0.02
A.......	Reddish brown friable silty clay containing some gray aggregates......	9–18	16.50	22.00	18.44	10.78	0.07
B.......	Grayish brown granular material having high bulk density............	0–10	17.61	9.90	39.40	19.60	0.08
B.......	Dark reddish brown clay having plastic gray nodules.................	10–25	10.31	11.00	46.60	10.40	0.07
C.......	Grayish purple soil material.........	0–25	17.73	9.70	53.20	17.00	0.34
C.......	Grayish purple concretions from slaglike material.....................	0–25	4.13	9.10	70.90	11.20	0.13
D......	Grayish purple soil material.........	0–24	17.32	1.42	57.44	20.56	0.15
D......	Grayish purple concretions from slaglike material.....................	0–24	2.60	6.10	72.82	11.18	0.08
E.......	Grayish purple soil material.........	0–30	17.21	8.70	46.40	18.90	0.20
E.......	Grayish purple concretions..........	0–30	3.89	12.00	65.70	11.40	0.14
F.......	Grayish purple soil.................	0–9	17.80	6.50	46.40	18.50	0.56
F.......	Grayish purple crystalline concretions.	0–9	2.41	8.30	71.50	13.40	0.11
F_1......	Grayish purple soil.................	9–30	20.20	6.20	47.66	19.40	0.30
F_1......	Grayish purple crystalline concretions.	9–30	3.60	3.30	74.60	12.40	0.13
G......	Grayish purple slaglike surface soil...	0–9	11.02	19.00	33.10	15.40	0.09
H......	Reddish brown granular surface soil..	0–20	12.38	16.00	37.60	10.20	0.10

TABLE 3
THE ANALYSIS OF SAMPLES OF SOIL FROM THE NAIWA SOIL FAMILY AREA OF MEYER LAKE, MOLOKAI, FOR TYPES OF IRON OXIDES IN ORDER TO CALCULATE THE POSSIBLE HYPOTHETICAL PERCENTAGE OF ILMENITE FROM THE FERROUS IRON AND TITANIUM OXIDE CONTENT

SAMPLING SITE	DEPTH INCHES	TOTAL Fe PER CENT	Fe_2O_3 PER CENT	FeO PER CENT	TiO_2 PER CENT	CALCULATED ILMENITE CONTENT	
						From TiO_2 PER CENT	From FeO PER CENT
A....................	0–9	25.3	20.8	14.8	13.7	26.0	31.2
A....................	9–18	22.1	15.8	12.6	4.3	8.2	26.6
B....................	0–10	31.7	29.3	12.2	17.3	32.8	25.8
B....................	10–25	34.6	32.5	13.1	6.0	11.5	27.8
D—soil..............	0–24	46.4	53.0	12.5	22.7	43.1	26.3
D—concretions........	0–24	50.4	68.4	4.1	9.8	18.6	8.6
F—soil...............	0–9	32.3	30.8	13.7	19.7	37.4	28.9
F—concretions........	0–9	50.2	68.4	3.3	10.9	20.6	7.0
G....................	0–9	39.4	48.6	7.0	18.9	35.8	14.7
H....................	0–20	34.6	36.6	12.0	14.7	28.0	25.3

occur in all of the samples. A much higher percentage of free titanium oxide occurs in the concretions. The data support the hypothesis that the primary titanium minerals break down in weathering to form a soluble form of titanium which is deposited and accumulated in concretions by weathering synthesis mechanism. Analysis by X-ray diffraction of similar soils has identified anatase, a secondary titanium oxide mineral. Further evidence of the occurrence of free titanium oxide and the weatherability of the primary titanium minerals can be obtained from the analysis of these samples for titanium oxide and ferrous oxide. The analysis of the surface soil of site A showed that this soil contained 13.7 per cent TiO_2. This amount of TiO_2 would require 15.1 per cent ferrous oxide to form ilmenite. The ferrous oxide content was found to be 14.8 per cent, which would mean that in this soil most of TiO_2 would exist as ilmenite with a small fraction of free titanium oxide. The results of analysis of the surface soil of the same sampling site indicate 22.7 per cent TiO_2 and 12.5 per cent ferrous oxide. The titanium content of this soil would require 25.1 per cent ferrous oxide to exist as ilmenite. The analysis of the soil shows that there is approximately 12 per cent free titanium oxide.

The data in Table 3 show a movement of iron in this deposit as shown by the high iron oxide content of the concretions. The ferric iron oxide content of the concretions was found to be 68 per cent as compared to a much lower content in the soil. The concretions have accumulated ferric oxide. The dehydrated soil has a higher content of ferric oxide than the soil of the hydrated soil area. The dehydrated soil and concretions are strongly magnetic, and as the concretions have a low ferrous oxide content the presence of maghemite is suggested. Sherman and Kanehiro (1954) reported similar observations in the analysis of concretions of the Naiwa family on Kauai.

The derived molecular ratios are given in Table 4 for some of the samples of this area. The silica to sesquioxide ratio of these samples ranged from 0.35 to 1.10 with the highest ratio occurring in the sample from the top of the slope. The silica to sesquioxide ratio of the concretions was found to be very low, 0.08 and 0.12. The silica to iron oxide (ferrous oxide + ferric oxide) ratio was found to be similar to the silica to sesquioxide ratio except that it was slightly higher. The ratio of ferrous oxide to titanium oxide was lower in the dehydrated soil area, which indicates that titanium oxide increased with dehydration.

TABLE 4

THE DERIVED MOLECULAR EQUIVALENT RATIOS FROM DATA GIVEN IN TABLES 2 AND 3 TO SHOW THE RELATIVE ACCUMULATION OF IRON AND TITANIUM OXIDES

SAMPLING SITE	DEPTH INCHES	DERIVED MOLECULAR RATIOS			
		$\frac{SiO_2}{R_2O_3}$	$\frac{SiO_2}{Fe_2O_3}$	$\frac{FeO}{TiO_2}$	$\frac{2\ FeO}{Fe_2O_3}$
A	0– 9	1.10	1.28	1.19	0.80
B	0–10	0.78	1.05	0.78	0.46
D—soil	0–24	0.67	0.69	0.61	0.26
D—concretions	0–24	0.12	0.13	0.46	0.07
F—soil	0–9	0.84	1.02	0.77	0.49
F—concretions	0–9	0.08	0.09	0.33	0.05
G	0–9	0.35	0.53	0.41	0.16
H	0–20	0.44	0.66	0.90	0.36

TABLE 5
CHEMICAL COMPOSITION OF SEDIMENTS FOUND ALONG THE SHORES OF MEYER LAKE, MOLOKAI

DESCRIPTION OF EROSIONAL MATERIALS	SiO_2 PER CENT	Al_2O_3 PER CENT	Fe_2O_3 PER CENT	TiO_2 PER CENT	MnO PER CENT
Silt from lake bottom	13.77	16.80	30.64	22.36	0.17
Coarse ferruginous concretions collected from shoreline of lake	8.62	9.50	46.70	20.56	0.07
Small pebbles found along shoreline	20.05	13.40	35.16	6.32	0.14

The ratio of ferrous oxide to ferric oxide was low in the soil samples, ranging from 0.16 to 0.80. This ratio was extremely low in the concretions, 0.05 and 0.07.

The data given in Table 5 were obtained from the analysis of the shoreline sediments of Meyer Lake. The silt from the lake bottom contained 22.36 per cent titanium oxide. The black crystalline minerals of titanium and iron oxides were easily identified in the water deposited silt. The coarse ferruginous concretions found at the foot of the slope, but on the shoreline where wave action could sort the material, contained 20.56 per cent titanium oxide. Other sorted soil aggregates having a lower specific gravity had a much lower titanium oxide content, 6.32 per cent. The iron oxide content of all of these materials was greater than 30 per cent. The silt material would have an appreciable amount of free titanium oxide.

SUMMARY

The titaniferous–ferruginous laterite areas in the Meyer Lake area of Molokai have been investigated to determine the nature of the weathering processes responsible for their development. The soils of this area belong to the Naiwa family of the ferruginous humic latosol group. These soils have accumulated iron and titanium oxides in the surface horizon. Indurate, concretionary, slaglike surface areas form on the slopes as a result of dehydration of the soil minerals. The concretion content of these indurate areas ranges from 30 to 43 per cent of the weight of the soil.

The soils of the indurate layer have a much higher content of titanium oxide and iron oxide than the hydrated friable soil in the adjacent areas. The highest content of iron oxide in the soil was 53 per cent and of titanium oxide, 21 per cent. The concretions were made up predominantly of iron oxide which amounted to as much as 72 per cent of the weight of the concretion. The titanium oxide content of the concretions ranges from 11 to 13 per cent. The occurrence of these oxides in concretions is conclusive evidence of their movement in soluble form, as the development of concretions can only be considered to be a product and a phase of weathering synthesis processes.

The fractionation of free titanium oxide and combined titanium was attempted through the analysis of these samples for ferrous oxide. The maximum possible content of ilmenite would be obtained when all of the ferrous oxide is assumed to occur in the mineral ilmenite. The data obtained by this analysis revealed that in the indurate soil and concretions, it was possible for appreciable quantities of titanium to exist as the free oxide. In some of the soil, at least half of the titanium existed as the free oxide, anatase.

The titanium and iron oxides accumulate in erosion sediments due to their specific gravity. There is a substantial difference between characteristics of the erosion deposits and the indurate layers.

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